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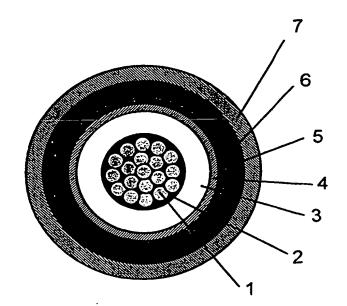
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(54) Title: ELECTRICAL CABLE HAVING A SEMICONDUCTIVE WATER-BLOCKING EXPANDED LAYER

(57) Abstract

Electrical cable, in particular for medium- or high-voltage power transmission or distribution, having a metal shield and a semiconductive water-blocking expanded layer. This layer exerts three main functions, the first one is to elastically and uniformly absorb radial forces of expansion and contraction of the cable coating layers due to thermal cycles of the cable during use, thus preventing deformations or breakages in the metal shield, the second one is to ensure electrical continuity between the cable core and the metal shield, the third one is to effectively avoid penetration and propagation of moisture and/or water along the cable core due, e.g., to possible ruptures in the metal shield. The third function is obtained by including in the expanded layer a water-swellable material.



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"ELECTRICAL CABLE HAVING A SEMICONDUCTIVE WATER-BLOCKING EXPANDED LAYER"

The present invention relates to an electrical cable, or high-voltage mediumparticular for in 5 semiconductive distribution, having a transmission or water-blocking expanded layer. In the present description, the term "medium voltage" is understood to refer to a voltage of between about 1 kV and about 30 kV, while the term "high voltage" is understood to refer to voltages 10 above 30 kV.

Cables for medium- or high-voltage power transmission or distribution generally consist of a metal conductor coated with a first inner semiconductive layer, an insulating layer and an outer semiconductive layer. For some uses, in particular when it needs to be watertight with respect to the exterior, the cable is enclosed inside a metal shield, usually an aluminium or copper shield, consisting of a continuous tube or a metal sheet shaped into a tube and welded or sealed so as to be watertight.

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During production, installation or use, breakages and piercings can occur in the metal shield, which allow penetration of moisture or even water into the cable core, with formation of electrochemical trees in the insulation layer, which can cause insulation failure.

A possible solution to this problem is provided in US Patent No. 4,145,567. A high-voltage cable is described the outside of the around therein having, semiconductive layer, a compressible layer of a foamed plastic material which should prevent external moisture layer, thus insulation the from reaching formation of electrochemical trees. According to that disclosure, the metal shield preferably maintains some pressure against the compressible layer so that no air or other fluid can travel along the interface between the compressible layer and the metal shield. As further insurance against passage of fluid along the cable, the metal shield can be bonded to the compressible layer. The compressible layer is preferably semiconducting.

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Ruptures in the metal shield may be caused by the thermal cycles to which the cable is subject as a result intensity of in the the daily variations of transported current, with corresponding variations in the cable temperature of between room temperature and the maximum operating temperature (for example between 20°C These thermal cycles cause dilation and 90°C). subsequent contraction of the coating layers of the cable, with consequent radial forces exerted on the metal shield. The metal shield can thus suffer mechanical deformations with formation of empty spaces between the shield and the outer semiconductive layer, which may give rise to nonuniformity in the electrical field. At the utmost, these the rupture of to lead deformations can particularly when it is welded or attached by means of sealing, and hence to complete loss of functionality of the shield.

A possible solution to this problem is provided in US Patent No. 5,281,757, where the metal shield is free to move with respect to the adjacent layers and has the overlapping edge portions bonded together by an adhesive which allows the overlapping edge portions to move relative to each other during the thermal cycling of the cable. A cushioning layer as that disclosed in the abovementioned US Patent No. 4,145,567 may be applied between the metal shield and the cable core. If desired, the cushioning layer may be a water swellable tape or a water swellable powder instead of a foamed plastic material.

According to the Applicant's experience, cable designs such as those described in US-4,145,567 and US-5,281,757 are not completely satisfactory. Firsly, the

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presence of a compressible layer between metal shield and cable core as disclosed in US-4,145,567 is not sufficient to effectively avoid penetration and propagation of moisture or water along the cable. In fact, to obtain an effective water-blocking effect, in US-5,281,757 suggested to use, instead of the compressible layer, a water-swellable tape or powder. However, the introduction of a water-swellable material under the metal shield would cause serious electrical problems. In fact, the metal shield, in addition to constituting a barrier against penetration of water and/or moisture, exerts important electrical functions and needs to be in electrical contact with the outer semiconductive layer. A first function of the metal shield is indeed to create a uniform radial electric field inside the cable and, simultaneously, to cancel out the electric field outside the cable. A further function is to support short-circuit currents.

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The presence of an insulating material such as a water-swellable material under the metal shield cannot ensure electrical continuity between the cable core and the metal shield. Moreover, from the point of view of production and handling, the use of water-swellable tapes or of free water-swellable powders has many drawbacks. Particularly, the use of a water-swellable tape involves an appreciable increase in costs and a decrease in productivity, since these tapes are expensive and imply the addition of a wrapping stage to the cable production process. On the other hand, the presence of free-flowing water-swellable powders makes production and installation of the cable quite cumbersome.

Finally, cables are known in the art which are designed to attenuate the effect of the thermal cycles on the metal shield and at the same time to avoid propagation of moisture and/or water along the cable. These cable are provided with an outer semiconductive layer with V-shaped

longitudinal grooves which are filled with a water-swellable material in the form of powder. The V-shaped geometry should ensure electrical contact between the semiconductive layer and the metal shield, on the one hand, and should assist the elastic recovery of the thermal dilations by the material which makes up the semiconductive layer, on the other hand.

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longitudinal these producing However, involves the use of a semiconductive layer thickness (about 2 mm or more), thereby increasing the cost and the overall weight of the cable. In addition, the desired geometry of the semiconductive layer is generally achieved by means of a precise process of extrusion in which appropriately designed dies are used. On the basis of the Applicant's experience, the formation of grooves of inevitable in practical terms, irregular geometry is, These geometrical process. an extrusion such irregularities can give rise to a non-uniform distribution of the pressure exerted on the metal shield and thus prevent the semiconductive layer from correctly carrying out its function of elastic absorption of the radial forces.

Therefore, the cables according to the above prior art cannot effectively address both the problem of avoiding penetration and propagation of moisture and/or water inside the cable core, and the problem of possible deformations or breakages of the metal shield due to the cable thermal cycles, while maintaining a proper electrical contact between metal shield and cable core.

The Applicant has now found the above problems can be effectively solved by inserting, under the metal shield, a layer of an expanded polymer material having semiconductive properties and including a water-swellable material. This layer is capable of elastically and uniformly absorbing radial forces of expansion and

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contraction due to the thermal cycles to which the cable is subjected during use, while ensuring the necessary electrical continuity between the cable and the metal shield. Moreover, the presence of the water-swellable material dispersed into the expanded layer is able to effectively block moisture and/or water, thus avoiding the use of water-swellable tapes or of free water-swellable powders.

In a first aspect, the present invention thus relates
to an electrical cable comprising a conductor, at least
one insulating layer, an outer metal shield and a layer of
an expanded polymer material placed under the said metal
shield, characterized in that the layer of the expanded
polymer material is semiconductive and includes a waterswellable material.

In the following, the "layer of an expanded polymer material" will be concisely indicated as "expanded layer".

In the present description and claims, the term "expanded polymer material" is understood to refer to a polymer material with a predetermined percentage of "free" space inside the material, i.e. of space not occupied by the polymer but by a gas or air.

In general, the percentage of free space in an expanded polymer is expressed in terms of the degree of expansion (G), which is defined by the following formula:

$$G = (d_0/d_e - 1) \cdot 100$$

where d_0 denotes the density of the non-expanded polymer and d_e denotes the apparent density measured on the expanded polymer.

The degree of expansion of the expanded layer according to the present invention can vary within a wide range, depending both on the specific polymer material used and on the thickness of the coating which it is intended to obtain. The degree of expansion is

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predetermined so as to ensure that the radial forces of thermal expansion and contraction of the cable are elastically absorbed and, simultaneously, so as to maintain the semiconductive properties. In general, the degree of expansion can range from 5% to 500%, preferably from 10% to 200%.

As regards the thickness of the expanded layer according to the present invention, this is equal to at least 0.1 mm; it is preferably between 0.2 and 2 mm and even more preferably between 0.3 and 1 mm. Thicknesses below 0.1 mm are difficult to produce in practice and, in any case, only allow a limited compensation for the deformation, while thicknesses above 2 mm, although not having any functional drawbacks in principle, can be used when any specific requirements might justify the increased cost.

According to a preferred aspect, the electrical cable according to the present invention also comprises a compact semiconductive layer placed between the insulating coating and the expanded layer.

The term "compact semiconductive layer" is understood to refer to a layer made of non-expanded semiconductive material, i.e. a material having a degree of expansion substantially null.

According to the Applicant's perception, this compact semiconductive layer can advantageously carry out the function of preventing partial discharging, and thus damage to the cable caused by any irregularities in the surface of interface between the insulating coating and the expanded layer. This function can be performed even by a very thin semiconductive layer, namely of about 0.1 mm or even less. However, from the practical point of view, a thickness of between 0.2 and 1 mm is preferable, and even more preferably between 0.2 and 0.5 mm.

As indicated above, the expanded layer includes a

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water swellable material. As shown by the tests carried out by the Applicant, the expanded layer is able to incorporate large amounts of water swellable material and the incorporated water-swellable material is capable of expanding when the expanded layer is placed in contact with moisture or water, thus efficiently performing its water-blocking function.

The water swellable material is generally in a subdivided form, particularly in the form of powder. The particles constituting the water-swellable powder have preferably a diameter not greater than 250 μ m and an average diameter of from 10 to 100 μ m. More preferably, the amount of particles having a diameter of from 10 to 50 μ m are at least 50% by weight with respect to the total weight of the powder.

The water-swellable material generally consists of a homopolymer or copolymer having hydrophilic groups along the polymer chain, for example: crosslinked and at least partially salified polyacrylic acid (for example the products Cabloc® from C. F. Stockhausen GmbH or Waterlock® from Grain Processing Co.); starch or derivatives thereof mixed with copolymers between acrylamide and sodium acrylate (for example products SGP Absorbent Polymer® from Henkel AG); sodium carboxymethylcellulose (for example the products Blanose® from Hercules Inc.).

To obtain an effective water-blocking action, the amount of water-swellable material to be included in the expanded layer is generally of from 5 to 120 phr, preferably of from 15 to 80 phr (phr = parts by weight with respect to 100 parts by weight of base polymer).

Figure 1 shows a cross-section of an embodiment of an electrical cable according to the present invention, of unipolar type, for medium-voltage power transmission.

This cable comprises a conductor (1), an inner semiconductive layer (2), an insulating layer (3), a

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compact semiconductive layer (4), an expanded layer (5), a metal shield (6) and an outer sheath (7).

The conductor (1) generally consists of metal wires, preferably made of copper or aluminium, which are braided together using conventional techniques. The metal shield (6), usually made of aluminium or copper, or also lead, consists of a continuous metal tube or of a metal sheet shaped into a tube and welded or sealed using an adhesive material so as to make it watertight. The metal shield (6) is usually coated with an outer sheath (7) consisting of a crosslinked or non-crosslinked polymer material, for example polyvinyl chloride (PVC) or polyethylene (PE).

The polymer material which constitutes the expanded layer can be any type of expandable polymer such as, for example: polyolefins, copolymers of different olefins, copolymers of an olefin with an ethylenically unsaturated ester, polyesters, polycarbonates, polysulphones, phenol resins, urea resins, and mixtures thereof. Examples of suitable polymers are: polyethylene (PE), in particular low density PE (LDPE), medium density PE (MDPE), high density PE (HDPE), linear low density PE (LLDPE), ultralow density polyethylene (ULDPE); polypropylene (PP); ethylene/propylene copolymers (EPR) elastomeric ethylene/propylene/diene terpolymers natural (EPDM); rubber; butyl rubber; ethylene/vinyl ester copolymers, for example ethylene/vinyl acetate (EVA); ethylene/acrylate copolymers, in particular ethylene/methyl acrylate (EMA), ethylene/ethyl acrylate (EEA) and ethylene/butyl acrylate ethylene/alpha-olefin thermoplastic copolymers; polystyrene; acrylonitrile/butadiene/styrene (ABS) resins; halogenated polymers, in particular polyvinyl chloride (PVC); polyurethane (PUR); polyamides; aromatic polyesters such as polyethylene terephthalate (PET) or polybutylene terephthalate (PBT); and copolymers thereof or mechanical mixtures thereof.

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Preferably, the polymer material is a polyolefin polymer or copolymer based on ethylene and/or propylene, and is chosen in particular from:

- (a) copolymers of ethylene with an ethylenically unsaturated ester, for example vinyl acetate or butyl acetate, in which the amount of unsaturated ester is generally between 5 and 80% by weight, preferably between 10 and 50% by weight;
- (b) elastomeric copolymers of ethylene with at least one C_3-C_{12} alpha-olefin, and optionally a diene, preferably 10 (EPR) or ethylene/propylene/diene ethylene/propylene generally having the following copolymers, (EPDM) composition: 35-90% mole of ethylene, 10-65% mole of alpha-olefin, 0-10% mole of diene (for example 1,4hexadiene or 5-ethylidene-2-norbornene); 15
 - (c) copolymers of ethylene with at least one C_4-C_{12} alpha-olefin, preferably 1-hexene, 1-octene and the like, and optionally a diene, generally having a density of between 0.86 and 0.90 g/cm³ and the following composition: 75-97% by mole of ethylene; 3-25% by mole of alpha-olefin; 0-5% by mole of a diene;
 - (d) polypropylene modified with ethylene/ C_3 - C_{12} alphaolefin copolymers, wherein the weight ratio between polypropylene and ethylene/ C_3 - C_{12} alpha-olefin copolymer is between 90/10 and 10/90, preferably between 80/20 and 20/80.

the commercial products Elvax® (Du For example, Pont), Levapren® (Bayer) and Lotryl® (Elf-Atochem) are in class (a), products Dutral® (Enichem) or Nordel® (Dow-Du Pont) are in class (b), products belonging to class (c) Exact® (Exxon), while (Dow-Du Pont) or Engage® ethylene/alpha-olefin. modified with polypropylene copolymers are commercially available under the brand names Moplen® or Hifax® (Montell), or also Fina-Pro® (Fina), and the like.

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particularly preferred are class (d), thermoplastic elastomers comprising a continuous matrix of a thermoplastic polymer, e.g. polypropylene, and fine particles (generally having a diameter of the order of 1-10 $\mu\text{m})$ of a cured elastomeric polymer, e.g. crosslinked EPR o EPDM, dispersed in the thermoplastic matrix. incorporated in be polymer may elastomeric uncured and state thermoplastic matrix the in dinamically crosslinked during processing by addition of a suitable amount of a crosslinking agent. Alternatively, the elastomeric polymer may be cured separately and then dispersed into the thermoplastic matrix in the form of fine particles. Thermoplastic elastomers of this type are described, e.g. in US-4,104,210 or EP-324,430. thermoplastic elastomers are preferred since they proved to be particularly effective in elastically absorb radial forces during the cable thermal cycles in the whole range of working temperatures.

Products known in the art for the preparation of semiconductive polymer compositions can be used to give semiconductive properties. material polymer particular, an electroconductive carbon black can be used, for example electroconductive furnace black or acetylene black, and the like. The surface area of the carbon black is generally greater than $20~\text{m}^2/\text{g}$, usually between 40~and500 m^2/g . Advantageously, a highly conducting carbon black may be used, having a surface area of at least $900 \text{ m}^2/\text{g}$, for example, the furnace carbon black such as, commercially under the tradename Ketjenblack® EC Chemie NV).

The amount of carbon black to be added to the polymer matrix can vary depending on the type of polymer and of carbon black used, the degree of expansion which it is intended to obtain, the expanding agent, etc. The amount of carbon black thus has to be such as to give the WO 99/33070 PCT/EP98/08284

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expanded material sufficient semiconductive properties, in particular such as to obtain a volumetric resistivity value for the expanded material, at room temperature, of less than 500 Ω ·m, preferably less than 20 Ω ·m. Typically, the amount of carbon black can range between 1 and 50% by weight, preferably between 3 and 30% by weight, relative to the weight of the polymer.

The compact semiconductive layer optionally present between the insulating coating and the expanded layer, as well as the inner semiconductive layer, both of compact type, are prepared according to known techniques, in particular by extrusion, the polymer material and the carbon black being selected from those mentioned above for the expanded layer.

insulating layer is preferably prepared by 15 extrusion of a polyolefin selected from those mentioned above for the expanded layer, in particular polyethylene, polypropylene, ethylene/propylene copolymers, the material is preferably After extrusion, for example known techniques, crosslinked 20 by peroxides or via silanes.

The expanded layer can be prepared by extrusion of the polymer material containing the semiconductive filler and the water-blocking material onto the core of the cable, i.e. the assembly of the conductor (1), inner semiconductive layer (2), insulating layer (3) and optional compact semiconductive layer (6). The cable core can itself also be prepared by extrusion, in particular by coextrusion of the three layers according to known techniques.

The polymer material can be mixed with the semiconductive filler, the water-swellable material and other optional conventional additives according to methods known in the art. The mixing can be carried out, for

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example, using an internal mixer of the type with tangential rotors (Banbury) or with interpenetrating rotors, or alternatively in continuous mixers such as those of the type Ko-Kneader (Buss), or of the type corotating or counter-rotating twin-screw.

The expansion of the polymer is normally carried out during the extrusion phase. This expansion can take place either chemically, by addition of a suitable expanding agent, i.e. one capable of evolving a gas under specific temperature and pressure conditions, or alternatively, physically, by high-pressure injection of gas directly into the extruder cylinder. The expanding agent preferably added to the polymer material only after addition of the fillers and other additives as described above and subsequent cooling of the mixture below the decomposition temperature of the expanding agent to avoid a premature expansion of the polymer. Particularly, the expanding agent can be advantageously added to the polymer composition during extrusion, e.g. through the extruder hopper.

Examples of suitable expanding agents are: azodicarbamide, para-toluenesulfonyl hydrazide, mixtures of organic acids (for example citric acid) with carbonates and/or bicarbonates (for example sodium bicarbonate), and the like.

Examples of gases to be injected at high pressure into the extruder cylinder are: nitrogen, carbon dioxide, air, low-boiling hydrocarbons, for example propane or butane, halogenated hydrocarbons, for example methylene chloride, trichlorofluoromethane, 1-chloro-1,1-difluoroethane, and the like, or mixtures thereof.

Preferably, the die in the extruder head will have a . diameter slightly smaller than the final diameter of the cable with expanded coating which it is intended to obtain, so that the expansion of the polymer outside the

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extruder allows to reach the desired diameter for the cable.

The selected extrusion temperature mainly depends on the nature of the polymer matrix, of the expanding agent and of the desired degree of expansion. Usually, an extrusion temperature not lower than 140°C is preferred to reach a sufficient degree of expansion.

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The expanded polymer material may or may not be crosslinked. The crosslinking can be carried out, after the extrusion and expansion phases, by known techniques, in particular by heating in the presence of a radical initiator, for example an organic peroxide such as dicumyl peroxide. Alternatively, a crosslinking can be carried out via silanes, which allows the use of a polymer such as those mentioned above, in particular a polyolefin, which are covalently bonded silane units comprising at least one hydrolysable group, for example trialkoxysilane particular trimethoxysilane groups. in grafting of the silane units can take place by radical for example with silane compounds, reaction dimethyldiethoxysilane, triethoxysilane, vinyldimethoxysilane, and the like. The crosslinking is carried out in the presence of water and a crosslinking catalyst, for example an organic titanate or a metal carboxylate. Dibutyltin dilaurate (DBTL) is particularly preferred.

Once the expanded layer has been prepared, the cable is enclosed inside the metal shield. According to a preferred embodiment, in the absence of applied forces, the diameter of the expanded layer is greater than the inside diameter of the metal shield, such as to obtain, after the metal shield has been applied, a predetermined degree of precompression of the expanded layer. This precompression makes it possible to achieve optimum contact between the expanded layer and the metal shield

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and can allow recovery of any residual deformation of the expanded layer, or else a certain degree of plastic deformation of the metal shield, during the phase of thermal contraction of the insulating layer.

Eventually, the metal shield can be coated with a protective sheath which can be obtained, for example, by extrusion of a polymer material, usually polyvinyl chloride or polyethylene.

A few illustrative examples will be given hereinbelow to further describe the invention.

EXAMPLES 1-2

Some mixtures suitable to form the expanded layer according to the present invention were prepared. The compositions are given in Table 1 (in phr). The components of the mixture were mixed together in a Banbury closed mixer (1.2 l working volume), loading first the base polymer, then, after a brief period of processing, the carbon black, the water swellable powder and the other additives (except the expanding agent).

The mixing was carried out for about 6 min with a final temperature for the extracted material of about 150°C. At the end of mixing the expanding agent was added to the mixture, the material being previously cooled to about 100°C in order to avoid a premature decomposition of the expanding agent, which would lead to uncontrolled expansion of the polymer. The mixture was then compression moulded at 160°C using a frame 200 x 200 mm in size and 3 mm in thickness. The mixture was added in amounts such as to obtain an initial layer 1 mm thick, so as to leave sufficient space for the polymer to expand. The following characteristics were measured on the test pieces thus obtained:

- apparent density, and then, knowing the density of the non-expanded material, degree of expansion was calculated according to the formula given above;

- volume resistivity at room temperature.

The data are given in Table 1.

were placed water: immediate in samples expansion of the water swellable powder up to a volume about three times the initial volume was observed.

EXAMPLE 3

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A medium-voltage cable was produced using the polymer composition of Example 1, according to the structure scheme reported in Fig. 1. The polymer composition was prepared according to Example 1, but without adding the expanding agent to avoid premature expansion of the The expanding agent was introduced only composition. during extrusion as described hereinbelow.

The cable core on which the expanded layer was to be deposited consisted of an aluminium conductor 70 mm² in with the following coated section, cross crosslinked vie peroxide on a catenary line:

- EPR layer made of semiconductive inner an containing carbon black (0.5 mm thick);
- an insulating layer made of EPR filled with kaolin (5.5 mm thick);
 - an outer semiconductive layer (compact) made of EVA containing 35% by weight of N472 carbon black (0.5 mm thick).
- To deposit the expanded layer on this cable core (having an outside diameter of about 23 mm), a 80 mm single-screw extruder in configuration 25 D was used. The extruder was equipped with an initial section of cylinder having longitudinal furrows, a box-type feed throat and a threaded discharge screw 25 D in length. The 30 depth of the screw groove was 9.6 mm in the supply zone and 7.2 mm in the final section, for an overall screw compression ratio of about 1:1.33.

electrically heated orthogonal extrusion head equipped with a conveyor belt with a double-suture line 35

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was used downstream of the extruder. The following die assembly was used: tip die 24 mm in diameter, ring compression die 24 mm in diameter. The tip die was chosen with the aim of allowing easy passage of the core to be coated, with a diameter about 1 mm greater than the diameter of the core to be coated. The ring die was, on the other hand, chosen with a diameter slightly smaller than the final diameter to be obtained, so as to prevent the material from expanding inside the extrusion head.

The following heat profile (°C) was used for the extruder and the extrusion head:

Feed	Screw	Zone	Zone	Zone	Zone	Zone	Zone	Collar	Head
throat		1	2	3	4	5	6		
20	neutral	160	170	180	185	190	195	200	200

The throughput speed of the core to be coated was set as a function of the desired thickness of expanded material. In our case, a line speed of 1.2 m/min was used. Under these conditions, the following extrusion parameters were recorded:

Extruder rotation speed: 1.2 rpm;

Hot semi-finished diameter: 25.0 mm;

Cold semi-finished diameter: 24.8 mm.

The semi-finished product was cooled in air. Direct contact with the cooling water was avoided so as not to incur problems of accidental re-swelling of the water-blocking powder. The semi-finished product obtained was subsequently wound on a reel.

The material was deposited on the core in a thickness of about 1 mm. This material was expanded chemically, by adding about 2% of the expanding agent Hydrocerol® CF 70 (carboxylic acid + sodium bicarbonate) into the extruder hopper.

The electrical conductivity and the degree of

expansion were measured on samples of the expanded layer thus obtained. The degree of expansion measured was about 20%.

Tests of expansion of the material in the presence of water (water-blocking effect) were also carried out: the material became swollen, by virtue of the presence of the water-swellable powder, up to a volume of about 3 times the initial volume.

EXAMPLE 4

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10 A thermoplastic elastomer was used as base material to produce an expanded layer according to the present invention. The composition is reported in Table 1 (inclusive of the expanding agent that was added only during extrusion). The mixing was carried out in the same 15 Banbury mixer as described for Examples 1-2 with a mixing time of about 10 min and a final temperature for the extracted material of about 195°C. After mixing, the material was granulated and sealed in plastic bags to avoid absorption of moisture.

EXAMPLE 5

A medium-voltage cable was produced using the polymer composition of Example 4, according to the structure scheme reported in Fig. 1.

The cable core consisted of an aluminium conductor having a 150 mm² cross section and a 14.0 mm diameter, coated with the following layers, crosslinked via peroxide on a catenary line:

- an inner semiconductive layer: product LE 0595 from Borealis (0.6 mm thick);
 - an insulating layer made of XLPE (4.65 mm thick);
- an outer semiconductive layer (compact): product LE 0595 from Borealis (0.4 mm thick).

The expanded layer was deposited on this core (having an outside diameter of about 25.3 mm) by extrusion according to the technique described in Example 3, using a

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30 mm single-screw extruder in configuration 24 D, a tip die of 25.7 mm diameter, a ring compression die of 26.1 mm diameter, and with the following thermal profile ($^{\circ}$ C):

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Feed	Screw	Zone 1	Zone 2	Zone 3	Collar	Head
throat 20	floating	190	200	210	200	200

The expanding agent was added during extrusion through the extruder hopper. The line speed was 2.9 m/min, with a screw speed of 56 rpm. The thickness of the expanded layer after extrusion and cooling was 0.65 mm.

The so obtained cable was then wrapped with a laquered aluminium stip (thickness: 0.2 mm) using an adhesive to bond the overlapping edges. Eventually, an external sheath made of PVC was applied by extrusion.

Two 3 m portion of the final cable were subjected to a test of penetration of water under thermal cycles according to Specification NF C 33-233 March 1998). After 50 mm) of the removal of a central portion (length: external coatings to reach the outer semiconductive layer (4), the cable specimens were immersed in water and kept at room temperature for 24 hours, then subjected to 10 thermal cycles of 8 hours each (4 hours of heating up to 100°C by circulating electrical current along conductor, then 4 hours of cooling). At the end of the test, water penetrated through the cutting for 20 cm at one side and for 25 cm at the other side, thus largely within the requirements of the specification (no water shall appear from the cable specimen extremities).

TABLE 1

EXAMPLE	1	2	4
Elvax® 470	100		
Elvax® 265		100	
Profax® PF 814			20
Santoprene® RC8001			80
Ketjenblack® EC 300	20	20	10
Irganox® 1010	0.5	0.5	0.2
Irganox® PS802			0.4
Waterlock® J550	40	40	25
Hydrocerol® CF70	2	2	2
d ₀ (g/cm ³)	1.15	1.15	1.012
d _e (g/cm ³)	0.95	0.95	0.86
Degree of expansion (%)	21	21	17.7
Volume resistivity $(\Omega \cdot m)$	<15	<15	2

Elvax® 470 (Du Pont): ethylene/vinyl acetate (EVA) copolymer (18% VA, melt index 0.7);

Elvax® 265 (Du Pont): EVA copolymer (28% VA, melt index
3.0);

Profax® PF 814 (Montell): isotactic propylene homopolymer
(MFI = 3 g/10' - ASTM D 1238);

Santoprene® RC8001 (Monsanto): thermoplastic elastomer (89%w cured EPR, 11%w polypropylene);

Ketjenblack® EC (Akzo Chemie): high-conductivity furnace
carbon black;

Waterlock® J550 (Grain Processing Co.): grounded

15 crosslinked polyacrylic acid (partially salified) (more than 50% by weight of particles having a diameter between 10 e 45 µm);

Hydrocerol® CF70 (Boeheringer Ingelheim): carboxylic acid/sodium bicarbonate expanding agent;

Irganox® 1010 : pentaerythryl-tetrakis[3-(3,5-di-tertbutyl-4-hydroxyphenyl)propionate] (Ciba-Geigy);

Irganox® PS802 FL: distearyl thiodipropionate (DSTDP)
(Ciba-Geigy).

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CLAIMS

- 1. Electrical cable comprising a conductor, at least one insulating layer, an outer metal shield and a layer of an expanded polymer material placed under the said metal shield, characterized in that the layer of the expanded polymer material is semiconductive and includes a waterswellable material.
- 2. Cable according to Claim 1, wherein the expanded layer has a predetermined degree of expansion so as to ensure elastic absorption of the radial forces of thermal expansion and contraction of the cable and to maintain the semiconductive properties.

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- 3. Cable according to Claim 2, wherein the degree of expansion of the expanded layer is between 5% and 500%.
- 4. Cable according to Claim 3, wherein the degree of 20 expansion of the expanded layer is between 10% and 200%.
 - 5. Cable according to any one of the preceding claims, wherein the thickness of the expanded layer is at least 0.1 mm.

- 6. Cable according to Claim 5, wherein the thickness of the expanded layer is between 0.2 and 2 mm.
- 7. Cable according to any one of the preceding 30 claims, also comprising a compact semiconductive layer placed between the insulating coating and the expanded layer.
- 8. Cable according to Claim 7, wherein the compact semiconductive layer has a thickness of from 0.1 to 1 mm.

9. Cable according to Claim 8, wherein the compact semiconductive layer has a thickness of from 0.2 to 0.5 mm.

- 10. Cable according to any one of the preceding claims, wherein the water-swellable material is in the form of powder.
- 11. Cable according to claim 10, wherein the water-swellable material is in the form of powder having a particle diameter not greater than 250 µm and an average particle diameter of from 10 to 100 µm.
- 12. Cable according to claim 11, wherein in the water-swellable material the amount of particles having a diameter of from 10 to 50 μ m are at least 50% by weight with respect the total weight of the powder.
- 20 13. Cable according to anyone of the previous claims, wherein the water swellable material is a homopolymer or copolymer having hydrophilic groups along the polymer chain.
- 25 14. Cable according to anyone of the previous claims, wherein the water-swellable material is present in an amount of from 5 to 120 phr.
- 15. Cable according to claim 14, wherein the water-30 swellable material is present in an amount of from 15 to 80 phr.
- 16. Cable according to any one of the preceding claims, wherein the polymer material which constitutes the expanded layer is an expandable polymer selected from:

polyolefins, copolymers of different olefins, copolymers of an olefin with an ethylenically unsaturated ester, polyesters, polycarbonates, polysulfones, phenolic resins, urea resins, and mixtures thereof.

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- 17. Cable according to Claim 16, wherein the polymer material is an olefin polymer or copolymer based on ethylene and/or propylene.
- 10 18. Cable according to Claim 17, wherein the polymer material is selected from:
 - (a) copolymers of ethylene with an ethylenically unsaturated ester, wherein the amount of unsaturated ester is between 5 and 80% by weight;
- (b) elastomeric copolymers of ethylene with at least one C_3-C_{12} alpha-olefin, and optionally a diene, having the following composition: 35-90% mole of ethylene, 10-65% mole of alpha-olefin, 0-10% mole of diene;
- (c) copolymers of ethylene with at least one C_4-C_{12} alpha-olefin, and optionally a diene, having a density of between 0.86 and 0.90 g/cm³;
 - (d) polypropylene modified with ethylene/ C_3 - C_{12} alphaolefin copolymers, wherein the weight ratio between polypropylene and ethylene/ C_3 - C_{12} alpha-olefin copolymer is between 90/10 and 10/90.
 - 19. Cable according to claim 18, wherein the polymer material is a thermoplastic elastomer comprising a continuous matrix of a thermoplastic polymer and fine particles of a cured elastomeric polymer dispersed in the thermoplastic polymer.
- 20. Cable according to any one of the preceding claims, wherein the expanded layer has a volumetric 35 resistivity value for the expanded material at room

temperature of less than 500 Ω ·m.

- 21. Cable according to any one of the preceding claims, wherein the expanded layer comprises a predetermined amount of electroconductive carbon black.
- 22. Cable according to Claim 21, wherein the electroconductive carbon black has a surface area of at least 20 $\rm m^2/\rm g$.

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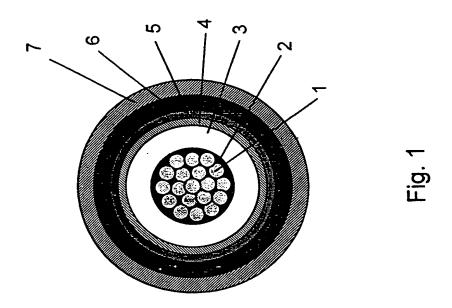
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- 23. Cable according to Claim 22, wherein the carbon black has a surface area of at least 900 \rm{m}^2/\rm{g} .
- 24. Cable according to any one of Claims 21 to 23, wherein the carbon black is present in amounts of between 5 and 80% by weight.
- 25. Cable according to Claim 24, wherein the carbon black is present in amounts of between 10 and 70% by 20 weight.
 - 26. Cable according to any one of the preceding claims, wherein the expanded layer is obtained by extrusion.

- 27. Cable according to Claim 26, wherein the expansion of the layer is obtained during the extrusion by addition of an expanding agent.
- 28. Cable according to Claim 26, wherein the expansion of the layer is obtained during extrusion by high-pressure injection of a gas.
 - 29. Cable according to any one of the preceding

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claims, wherein the diameter of the expanded layer, in the absence of applied forces, is greater than the inside diameter of the metal shield, so as to obtain a predetermined degree of precompression of the expanded layer after the metal shield has been applied.



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A. CLASSII	FICATION OF SUBJECT MATTER		
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B. FIELDS	SEARCHED		
	cumentation searched (classification system followed by classification	n symbols)	
IPC 6	H01B	,	
			1
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Electronic di	ata base consulted during the international search (name of data bas	e and, where practical search terms used)	
			-
C DOCUM	ENTS CONSIDERED TO BE RELEVANT		
			
Category *	Citation of document, with indication, where appropriate, of the rele	ivant passages	Relevant to claim No.
Α	US 4 145 567 A (BAHDER ET AL.)		1,2,7,
	20 March 1979		16-18
	see column 2, line 35 - column 5,	line 68:	
	figure 1	1	
Α	EP 0 116 754 A (CABLE TECHNOLOGY		1,2,7
[''	LABORATORIES) 29 August 1984		*, -, '
	see page 7, line 34 - page 13, li	ne 4·	
	figure 1		
Α	EP 0 577 233 A (SIEMENS) 5 Januar	v 1994	1,7,10
^ `	see column 2, line 1 - line 27; f	igures	1,7,10
1	1,2	iguies	
	·	į	
ĺ			
		1	
Furt	ther documents are listed in the continuation of box C.	X Patent family members are listed	in annex.
* Special ca	stegories of cited documents :	"T" later document published after the inte	mational filing date
"A" docum	ent defining the general state of the art which is not	or priority date and not in conflict with	the application but
consi	dered to be of particular relevance	cited to understand the principle or the invention	eory underlying the
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"P" docum	ent published prior to the international filing date but than the priority date claimed	in the art. "8" document member of the same patent	tamily
			
Date of the	actual completion of the international search	Date of mailing of the international sea	arch report
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1	22 April 1999	03/05/1999	
Name and	mailing address of the ISA	Authorized officer	· · · · · · · · · · · · · · · · · · ·
	European Patent Office, P.B. 5816 Patentiaan 2	Authorized officer	
1	NL - 2280 HV Rijswijk		
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Information on patent family members

enternatic Application No PCT/EP 98/08284

	Patent document cited in search report		Publication date	Patent family member(s)	Publication date
_	US 4145567	Α	20-03-1979	NONE	
	EP 116754	Α	29-08-1984	BR 8307059 A JP 59148210 A US 4533789 A	13-11-1984 24-08-1984 06-08-1985
	EP 577233	Α	05-01-1994	DE 9208880 U AT 133809 T CZ 9301228 A DE 59301532 D SK 66293 A	19-11-1992 15-02-1996 16-02-1994 14-03-1996 02-02-1994

International Application No PCT/US 02/39416

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 H0189/02 H018 H01B13/14 According to International Patent Classification (IPC) or to both national classification and IPC Minimum documentation searched (classification system followed by classification symbols) IPC 7 H01B Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ C. DOCUMENTS CONSIDERED TO BE RELEVANT Category ° Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. Α EP 0 707 322 A (ALCATEL CABLE) 1 - 4817 April 1996 (1996-04-17) column 3, line 16 -column 5, line 7; figures 1,2 US 4 145 567 A (EAGER JR GEORGE S ET AL) Α 1 - 4820 March 1979 (1979-03-20) cited in the application column 2, line 35 -column 7, line 30; figures 1-3 Α WO 99 33070 A (CAIMI LUIGI ; BALCONI LUCA 1 - 48(IT); BAREGGI ALBERTO (IT); BELLI SERGIO) 1 July 1999 (1999-07-01) cited in the application abstract; figure 1 Further documents are listed in the continuation of box C. Patent family members are listed in annex. Special categories of cited documents: *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the 'A' document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docu-*O* document referring to an oral disclosure, use, exhibition or other means ments, such combination being obvious to a person skilled document published prior to the international filing date but later than the priority date claimed in the art. "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 19 August 2003 26/08/2003 Name and mailing address of the ISA Authorized officer European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Demolder, J Fax: (+31-70) 340-3016

Information on patent family members

International Application No PCT/US 02/39416

Patent document cited in search report		Publication [*] date		Patent family member(s)	Publication date
EP 0707322	Α	17-04-1996	FR	2725555 A1	12-04-1996
			CA	2160064 A1	12-04-1996
			EP	0707322 A1	17-04-1996
			JP	8115620 A	07-05-1996
US 4145567	Α	20-03-1979	NONE		
WO 9933070	 А	01-07-1999	IT	MI972839 A1	22-06-1999
			ΑT	241204 T	15-06-2003
			AU	743935 B2	07-02-2002
			AU	2274199 A	12-07-1999
			BR	9814391 A	10-10-2000
			CA	2315694 A1	01-07-1999
			CN	1306668 T	01-08-2001
			DE	69814921 D1	26-06-2003
			WO	9933070 A1	01-07-1999
			EP	1042763 A1	11-10-2000
			HU	0100055 A2	28-05-2001
		-	JP	2001527267 T	25-12-2001
			SK	9352000 A3	11-06-2001
			TR	200001922 T2	22-01-2001
			US	6455769 B1	24-09-2002
			ZA	9811632 A	06-10-1999